Preparation of a Highly Alkyl-substituted Bis(8-hydroxyquinoline) Derivative and Its Use for the Self-Assembly of a Lipophilic Helicate with an Internal Binding Site for Cationic Guests

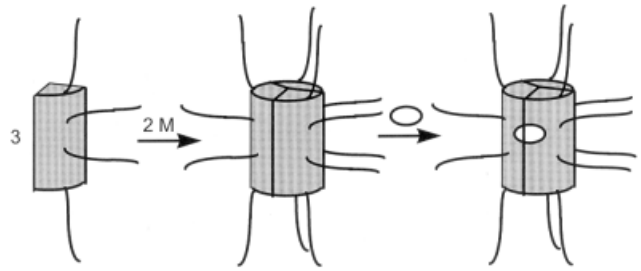
Markus Albrecht,*[a] Oliver Blau,[a] and Jeanette Zauner[a]

Keywords: 8-Hydroxyquinoline / Gallium / Cryptands / Self-assembly / Host-guest chemistry

The tetra-decyl-substituted ethylene-linked bis(8-hydroxyquinoline) derivative **9-H$_2$** is synthesized in an eight step procedure starting from 3-*n*-decyl-8-methoxyquinoline (**1**). NBS-bromination followed by a Suzuki-reaction enables the introduction of a decyl chain in the 5-position. In the key step of the sequence a mild $(Ph_3P)_2NiBr_2$-catalyzed homocoupling reaction of the benzyl bromide **7** is performed. In the presence of cationic templates (M^+ = Na^+, K^+, NH_4^+) compound **9-H$_2$** reacts with gallium(III) ions to form dinuclear complexes $[M\subset\{(\mathbf{9})_3Ga_2\}]Cl$ in template-directed self-assembly processes. For the first time helicate-type cryptates are obtained which show good solubility in apolar solvents.

Introduction

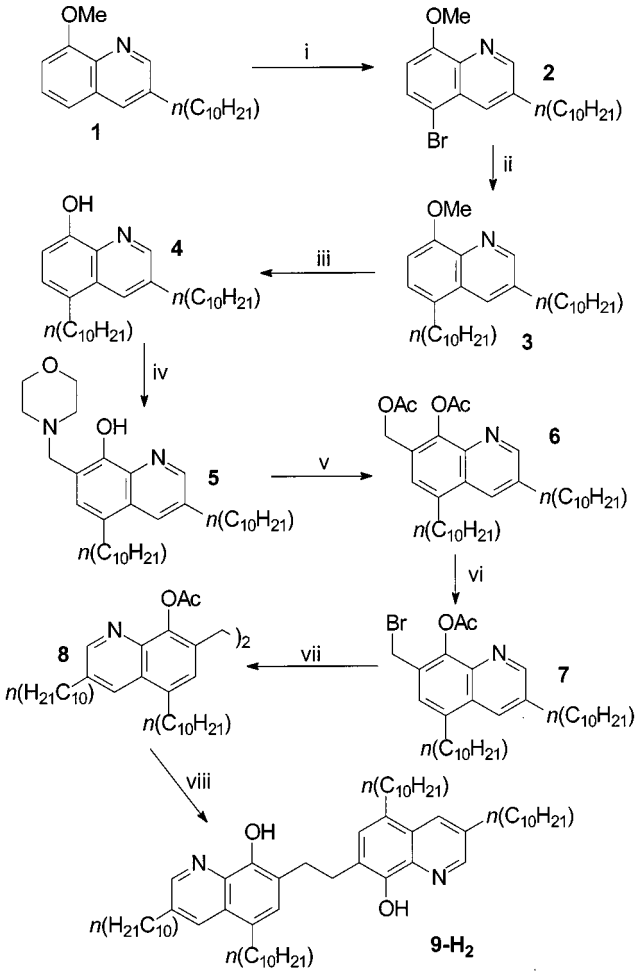
Triple-stranded helicate-type complexes are formed by the self-assembly of three linear oligo-donor ligands and two (or more) metal ions. In this process three organic building-blocks are brought together by coordination to the metal ions to form one "cylindrical" supramolecular aggregate[1] which can eventually bind small molecules or ions in its interior.[2–4] Due to the high charge of the helicates their chemistry is restricted to polar solvents. Only a few neutral complexes have been previously described which possess low solubility in common solvents.[2,4,5]



Scheme 1. Schematic presentation of the metal-directed self-assembly of highly alkyl-substituted helicate-type coordination compounds and the inclusion of appropriate guest species

Attachment of long side chains to the periphery of the organic ligands upon complex formation leads to supramolecular aggregates which possess an outer core with specific properties, while the internal polar binding site remains (Scheme 1). This concept should be useful in, for example, the one step formation of dendrimers by self-assembly of helicate-type structures from three ligands which bear dendritic side chains.[6]

In a recent study we showed, that dinuclear gallium(III) helicates which bear six decyl substitutents can be dissolved



Scheme 2. Synthesis of the ethylene-bridged bis(8-hydroxyquinoline) ligand **9-H$_2$**: i) NBS, $CHCl_3$ (quant.); ii) 9-*n*-decyl-9-borabicyclononane (freshly prepared from 1-decene and 9-BBN), NaOH, $(dppf)PdCl_2$ (84%); iii) HBr, H_2O (quant.); iv) morpholine, formaline (90%); v) acetic anhydride (quant.); vi) HBr/HOAc (66%); vii) $(Ph_3P)_2NiBr_2$, Et_4NI, activated zinc (45%); viii) trifluoroacetic acid (quant.)

[a] Institut für Organische Chemie, Universität Karlsruhe, Richard-Willstätter-Allee, D-76131 Karlsruhe, Germany
Fax: (internat.) + 49-721/698529
E-mail: albrecht@ochhades.chemie.uni-karlsruhe.de

  1434–193X/99/1111–3165 $ 17.50+.50/0

in chloroform (approximately 2 g/L).[4] To improve the solubility in apolar solvents and to make the compounds available for organic chemistry, we now present the synthesis, coordination properties and host/guest chemistry of the highly alkyl-substituted ethylene-bridged bis(8-hydroxyquinoline) ligand **9-H$_2$**.

Results and Discussion

Synthesis of the Bis(8-hydroxyquinoline) Derivative 9-H$_2$

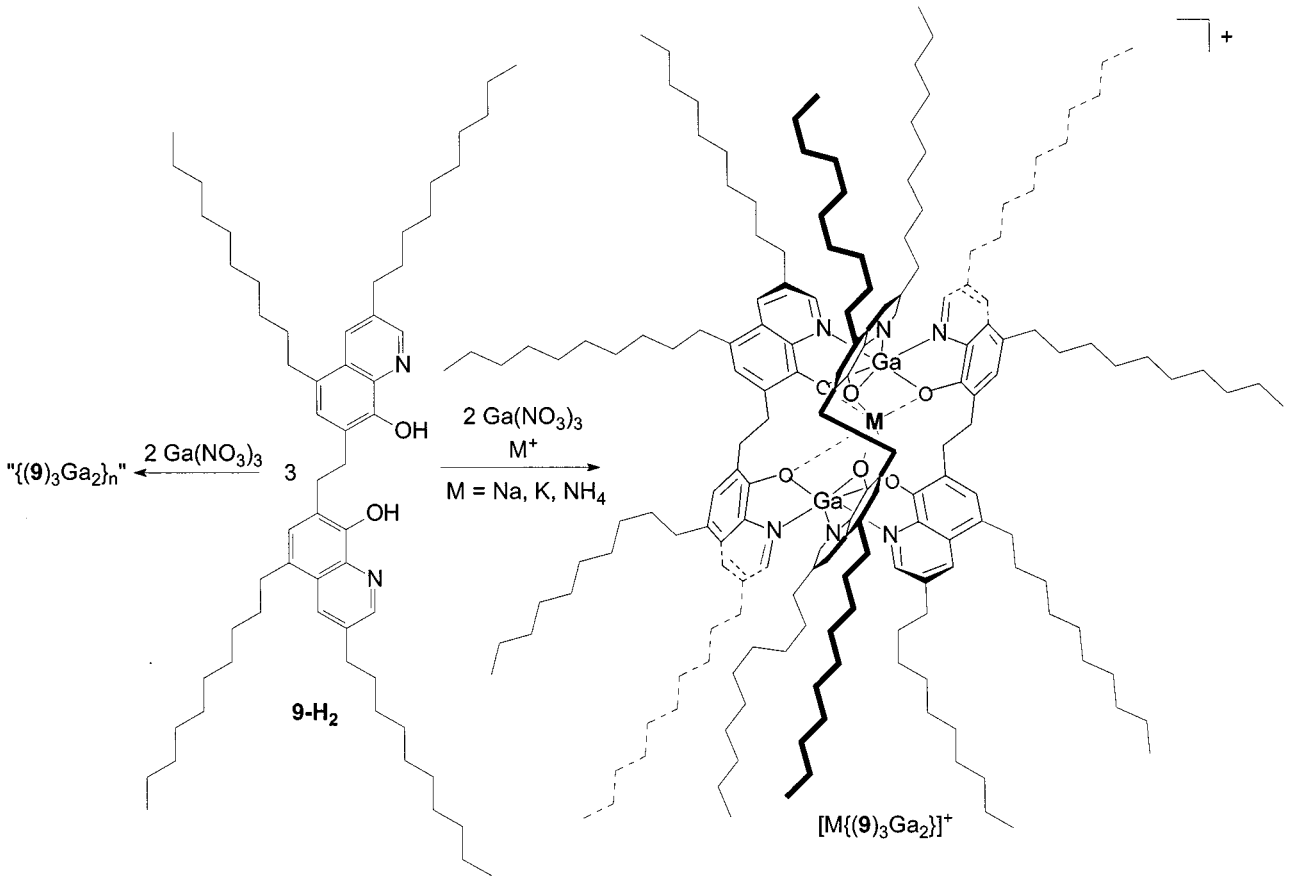
For the preparation of highly alkyl-substituted (8-hydroxyquinoline) derivatives a strategy had first to be developed to allow the attachment of two *n*-decyl chains to the hydroxyquinoline moiety (3- and 5-position). The first alkyl-substituent is introduced during the formation of 3-*n*-decyl-8-methoxyquinoline (**1**) by the Skraup reaction.[4b]

To introduce the second substituent the methoxyquinoline derivative **1** is selectively brominated with NBS (*N*-bromosuccinimide) to obtain compound **2** (quantitative)[7] and an *n*-decyl group is attached by Suzuki-coupling of 9-*n*-decyl-9-borabicyclononane (formed in situ) with **2** in the presence of NaOH and (dppf)PdCl$_2$ (84% of **3**).[8] The bis(*n*-decyl)methoxyquinoline derivative **3** is transformed into **4** by cleavage of the methyl ether with HBr (quantitative). Subsequent reaction with formaline and morpholine introduces, in a Mannich-type reaction, an *N*-morpholinomethyl substituent in the 7-position of the quinoline moiety (90% of **5**). In a reaction with acetic anhydride the morpholino group is quantitatively substituted by acetate and the hydroxy function is protected (**6**). Addition of HBr/HOAc to **6** followed by work up with acetic anhydride affords the benzyl bromide **7**.[4,7,9] In the critical reaction step of this sequence the bromide **7** is coupled in 45% yield using the mild homo-coupling catalyst (Ph$_3$P)$_2$NiBr$_2$ in the presence of activated Zn and tetraethylammonium iodide.[10] Finally the ligand **9-H$_2$** is obtained quantitatively by removal of the protecting groups with TFA (trifluoroacetic acid).

Coordination Studies

The bis(8-hydroxyquinoline) derivative **9-H$_2$** is ideal for the formation of neutral supramolecular gallium(III) complexes.[11] As observed earlier for similar systems, no well-defined neutral coordination compound is formed by reaction of **9-H$_2$** with gallium(III) nitrate. NMR spectroscopy ($CDCl_3$) of the soluble material shows that a mixture of different isomers, oligomers, and/or polymers "{(**9**)$_3$Ga$_2$}$_n$" is probably obtained (Scheme 3).[4,12,13]

In the presence of MCl (M = Na, K, NH$_4$) the cryptates [M⊂{(**9**)$_3$Ga$_2$}]$^+$ are obtained in a template-directed self-



Scheme 3. Formation of gallium(III) complexes from **9-H$_2$**

assembly process. The reaction is performed in a mixture of dichloromethane, methanol and water (15:5:1) to guarantee the solubility of all reactants. In contrast to the analogous complexes which were described earlier,[4] the cryptates $[M\subset\{(\mathbf{9})_3Ga_2\}]Cl$ can be easily dissolved in solvents like chloroform, dichloromethane, benzene, ether, or even hexane.

In the positive FAB-MS spectrum peaks for the alkali metal cryptates are observed at *m/z* = 2786 $[Na\subset\{(\mathbf{9})_3Ga_2\}]^+$ and 2804 $[K\subset\{(\mathbf{9})_3Ga_2\}]^+$. No positive FAB-MS can be obtained for $[\{NH_4\}\subset\{(\mathbf{9})_3Ga_2\}]^+$. The ^1H NMR spectra of $[M\subset\{(\mathbf{9})_3Ga_2\}]Cl$ show, besides the signals of the alkyl substituents, resonances for the diastereotopic spacer protons at δ = 3.40 and 2.62 (hidden under alkyl signal for M = Na), 3.28 and 2.66 (hidden under alkyl signal for M = K), or 3.25 and 2.64 (M = NH_4). The aromatic protons also lead to characteristic signals: while the shifts of the proton H^4 (δ ≈ 8.30) and H^6 (δ ≈ 7.44) do not change significantly when changing the cation, the chemical shift of proton H^2 is highly dependent on the guest cation which is bound in the interior of the dinuclear gallium cryptand [δ(H^2) = 6.85 (Na), 7.45 (K), 7.67 (NH_4)]. The cryptand $\{(\mathbf{9})_3Ga_2\}$ adjusts its size to that of the cation by using its gallium complex units as molecular hinges and thereby forces H^2 to experience different anisotropic shifts. This observation is in accordance with our earlier results.[4] For the ammonium salt $[\{NH_4\}\subset\{(\mathbf{9})_3Ga_2\}]Cl$ a broad signal is observed at δ = 8.32 (4 H) which corresponds to the encapsulated ammonium cation.

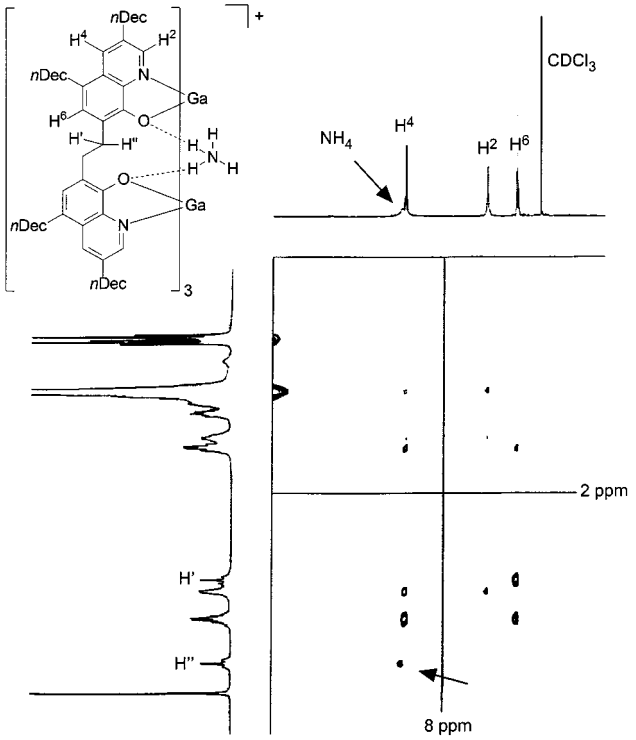


Figure 1. Part of the ROESY NMR spectrum of $[\{NH_4\}\subset\{(\mathbf{9})_3Ga_2\}]Cl$ in $CDCl_3$; the crosspeak between the NH_4-signal and the resonance of the spacer proton H′′ is marked with an arrow.

A part of the ROESY NMR spectrum of $[\{NH_4\}\subset\{(\mathbf{9})_3Ga_2\}]Cl$ in $CDCl_3$ is presented in Figure 1. The spectrum clearly shows the cross peak between the signal of the encapsulated ammonium cation and the spacer proton H′′. The second proton of the spacer H′ is pointing away from the cryptand and consequently does not show a cross peak with NH_4^+ but leads to a strong coupling with the aromatic proton H^6.

Conclusion

We have developed a strategy for the synthesis of the highly substituted 8-hydroxyquinoline ligand **9-H**$_2$ and used it for the formation of cryptate-type helicates with novel solubility properties. NBS-bromination followed by Suzuki-coupling has proved to be a very useful method for the functionalization of the 8-hydroxyquinoline skeleton in the 5-position. As observed earlier for related systems, **9-H**$_2$ with gallium(III) ions and MCl (M = Na, K, NH_4) forms the helicates $[M\subset\{(\mathbf{9})_3Ga_2\}]Cl$ in a template-directed self-assembly process. Thus, cryptate-type complexes were obtained in which the polar internal cavity is embedded in an apolar "greasy" outer core of alkyl-chains. ROESY NMR spectroscopy of the NH_4^+-cryptate reveals that the cation is located in the interior of the supramolecular aggregate. The positively charged metalla-cryptates show good solubility in apolar organic solvents like chloroform, dichloromethane, ether, benzene, or hexane. Therefore they are potential candidates for phase transfer catalysis or for the preparation of dendrimer-type complexes.

Experimental Section

General Remarks: Melting points were measured on a Büchi 535 (uncorrected). IR spectra were obtained on a Bruker IFS 88 spectrometer (diffuse reflection, KBr). EI MS/HRMS (70 eV) or FAB MS spectra {matrix: 3-nitrobenzoic acid (3-NBA)} were detected on a Finnigan MAT 90 spectrometer. For ^1H NMR and ^{13}C NMR (BB/DEPT) a Bruker DRX 500 or a AM 400 spectrometer were used (internal standard: $CHCl_3$). UV-Vis spectra were obtained on a Perkin−Elmer UV-Vis Lambda 2 spectrometer.

5-Bromo-3-*n*-decyl-8-methoxyquinoline (2): 3-*n*-Decyl-8-methoxyquinoline[4a] (**1**, 1.00 g, 3.34 mmol) and *N*-bromosuccinimide (NBS, 1.19 g, 6.64 mmol) were stirred for 2 h in chloroform (10 mL). The organic phase was washed with water (3 × 50 mL), dried ($MgSO_4$) and solvent was evaporated. Yield: 1.26 g (100%) of **2** as a brown solid; m.p.: 55°C. − ^1H NMR ($CDCl_3$, 296 K): δ = 8.77 (d, *J* = 2.1 Hz, 1 H), 8.20 (d, *J* = 2.1 Hz, 1 H), 7.67 (d, *J* = 8.4 Hz, 1 H), 6.85 (d, *J* = 8.4 Hz, 1 H), 4.05 (s, 3 H), 2.82 (t, *J* = 7.7 Hz, 2 H), 1.71 (m, 2 H), 1.31 (m, 14 H), 0.86 (t, *J* = 6.9 Hz, 3 H). − ^{13}C NMR ($CDCl_3$, 296 K): δ = 155.3 (C), 151.3 (CH), 139.3 (C), 137.5 (C), 133.6 (CH), 130.0 (CH), 128.1 (C), 111.5 (C), 107.2 (CH), 56.1 (CH_3), 33.2 (CH_2), 31.9 (CH_2), 31.1 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 29.2 (CH_2), 28.7 (CH_2), 22.7 (CH_2), 14.1 (CH_3). − IR (KBr): $\tilde{\nu}$ = 2953, 2921, 2848, 1495, 1461, 1361, 1313, 1250, 1099, 819, 793 cm^{-1}. − MS (EI, 70 eV); *m/z* (%): = 379 (100) $[M]^+$. − HRMS calcd. for $C_{20}H_{28}BrNO$: 377.1354, found: 377.1342. − $C_{20}H_{28}BrNO$: calcd. C 63.49, H 7.46, N 3.70; found C 62.96, H 7.50, N 3.52.

3,5-Bis(*n*-decyl)-8-methoxyquinoline (3): 1-Decene (1.10 g, 7.85 mmol) was dissolved in THF at 0°C and a 0.5 M solution of 9-BBN (15.7 mL, 7.85 mmol) in THF was added. After 5 h at room temp. a 3 M NaOH solution (7.2 mL, 21.6 mmol), (dppf)$PdCl_2$ (174 mg, 0.22 mmol), bromide **2** (2.70 g, 7.15 mmol) and 20 mL of THF were added. The mixture was refluxed for 15 hours and the phases were separated. The organic phase was evaporated to dryness and the crude product was purified by column chromatography (silica gel, hexane/ethyl acetate 5: 1). Yield: 2.65 g (84%) of **3** as a yellow oil. − ^{1}H NMR ($CDCl_3$, 296 K): δ = 8.78 (s, 1 H), 8.04 (s, 1 H), 7.25 (d, *J* = 7.9 Hz, 1 H), 6.90 (d, *J* = 7.9 Hz, 1 H), 4.06 (s, 3 H), 2.94 (t, *J* = 7.7 Hz, 2 H), 2.81 (t, *J* = 7.6 Hz, 2 H), 1.71 (m, 4 H), 1.33 (m, 28 H), 0.88 (m, 6 H). − ^{13}C NMR ($CDCl_3$, 296 K): δ = 153.7 (C), 150.0 (CH), 138.8 (C), 135.4 (C), 130.8 (C), 130.1 (CH), 127.7 (C), 126.0 (CH), 106.2 (CH), 55.8 (CH_3), 33.4 (CH_2), 31.9 (3 CH_2), 31.3 (CH_2), 30.9 (CH_2), 29.6 (4 CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 29.2 (CH_2), 29.1 (CH_2), 22.7 (3 CH_2), 14.1 (2 CH_3). − IR (KBr): $\tilde{\nu}$ = 2925, 2854, 1467, 1412, 1325, 1299, 1164, 720, 677 cm^{-1}. − MS (EI, 70 eV); *m/z* (%): = 439 (0.3) $[M]^+$. − HRMS calcd. for $C_{30}H_{49}NO$: 439.3814, found: 439.3789.

3,5-Bis(*n*-decyl)-8-hydroxyquinoline (4): The methyl ether **3** (210 mg, 0.48 mmol) was refluxed in 20 mL of aqueous HBr (48%) for 15 h. By addition of aqueous KOH the mixture was neutralized and subsequently extracted with dichloromethane (3 × 50 mL). The organic phase was dried ($MgSO_4$) and solvent was removed in vacuum. Yield: 204 mg (100%) of **4** as a green, hygroscopic solid; m.p. 92−93°C. − ^{1}H NMR ($CDCl_3$, 296 K): δ = 8.63 (s, 1 H), 8.07 (s, 1 H), 7.24 (d, *J* = 7.7 Hz, 1 H), 7.04 (d, *J* = 7.7 Hz, 1 H), 2.93 (t, *J* = 7.7 Hz, 2 H), 2.82 (t, *J* = 7.7 Hz, 2 H), 1.70 (m, 4 H), 1.34 (m, 28 H), 0.88 (m, 6 H). − ^{13}C NMR ($CDCl_3$, 296 K): δ = 150.3 (C), 148.6 (CH), 137.0 (C), 135.7 (C), 131.4 (CH), 128.8 (C), 127.1 (CH), 126.9 (C), 108.6 (CH), 33.6 (CH_2), 31.9 (2 CH_2), 31.8 (CH_2), 31.4 (2 CH_2), 31.2 (CH_2), 29.7 (2 CH_2), 29.6 (3 CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.3 (2 CH_2), 29.2 (CH_2), 22.7 (2 CH_2), 14.1 (2 CH_3). − IR (KBr): $\tilde{\nu}$ = 3310, 2954, 2918, 2850, 1497, 1468, 1423, 1225, 676 cm^{-1}. − MS (EI, 70 eV); *m/z* (%): = 425 (100) $[M]^+$. − HRMS calcd. for $C_{29}H_{47}NO$: 425.3658, found: 425.3667. − $C_{29}H_{47}NO{\cdot}0.25H_2O$: calcd. C 80.97, H 11.13, N 3.26; found C 81.26, H 10.67, N 3.55.

3,5-Bis(*n*-decyl)-8-hydroxy(7-*N*-morpholinomethyl)quinoline (5): Quinoline **4** (190 mg, 0.45 mmol) was dissolved in a mixture of ethanol (10 mL)/dichloromethane (15 mL). Morpholine (0.09 mL, 0.98 mmol) and formalin (0.12 mL, 1.78 mmol) were added and the mixture was stirred for 15 h at 40°C before the solvent was removed in vacuo. The crude product was purified by column chromatography (silica gel, gradient: dichloromethane → dichloromethane/methanol 49:1). Yield: 210 mg (90%) of **5** as a brown solid; m.p. 48−49°C. − ^{1}H NMR ($CDCl_3$, 296 K): δ = 8.65 (d, *J* = 1.6 Hz, 1 H), 7.95 (d, *J* = 1.6 Hz, 1 H), 7.03 (s, 1 H), 3.77 (s, 2 H), 3.72 (t, *J* = 4.4 Hz, 4 H), 2.86 (t, *J* = 7.7 Hz, 2 H), 2.74 (t, *J* = 7.6 Hz, 2 H), 2.56 (br s, 4 H), 1.63 (m, 4 H), 1.25 (m, 28 H), 0.83 (m, 6 H). − ^{13}C NMR ($CDCl_3$, 296 K): δ = 150.4 (C), 149.6 (CH), 137.8 (C), 134.9 (C), 130.4 (CH), 128.1 (C), 127.4 (CH), 126.4 (C), 115.7 (C), 66.7 (2 CH_2), 59.8 (CH_2), 53.0 (2 CH_2), 33.3 (CH_2), 31.8 (2 CH_2), 31.6 (CH_2), 31.2 (CH_2), 31.0 (CH_2), 29.5 (5 CH_2), 29.4 (CH_2), 29.3 (CH_2), 29.2 (2 CH_2), 29.0 (CH_2), 22.5 (2 CH_2), 14.1 (2 CH_3). − IR (KBr): $\tilde{\nu}$ = 3277, 2923, 2852, 1468, 1422, 1379, 1293, 1158, 1108, 1073, 860, 722 cm^{-1}. − MS (EI, 70 eV); *m/z* (%): = 524 (1) $[M]^+$, 439 (100). − HRMS calcd. for $C_{34}H_{56}N_2O_2$: 524.3658, found: 524.3667. − $C_{34}H_{56}N_2O_2$: calcd. C 77.81, H 10.76, N 5.34; found C 76.73, H 10.31, N 5.33.

8-Acetoxy-7-(acetoxymethyl)-3,5-bis(*n*-decyl)quinoline (6): The morpholine derivative **5** (180 mg, 0.34 mmol) was refluxed in acetic anhydride (5 mL) for 15 h. The solvent was evaporated in vacuum and the residue was dissolved in dichloromethane (30 mL) and washed with saturated aqueous $NaHCO_3$ (3 × 30 mL). The organic phase was dried over $MgSO_4$ and the solvent was removed in vacuum. Yield: 185 mg (100%) of **6** as a brown oil. − ^{1}H NMR ($CDCl_3$, 296 K): δ = 8.75 (s, 1 H), 8.04 (s, 1 H), 7.37 (s, 1 H), 5.24 (s, 2 H), 2.99 (t, *J* = 7.9 Hz, 2 H), 2.79 (t, *J* = 7.7 Hz, 2 H), 2.50 (s, 3 H), 2.21 (s, 3 H), 1.69 (m, 4 H), 1.32 (m, 28 H), 0.87 (m, 6 H). − ^{13}C NMR ($CDCl_3$, 296 K): δ = 170.8 (C), 169.7 (C), 169.2 (C), 151.7 (CH), 144.0 (CH), 137.0 (CH), 135.8 (C), 130.8 (CH), 127.8 (C), 126.8 (CH), 126.5 (C), 61.4 (CH_2), 33.4 (CH_2), 32.2 (CH_2), 31.9 (2 CH_2), 31.1 (CH_2), 30.9 (CH_2), 29.7 (CH_2), 29.6 (4 CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.3 (2 CH_2), 29.1 (CH_2), 22.7 (2 CH_2), 22.2 (CH_3), 22.1 (CH_3), 14.1 (CH_3). − IR (KBr): $\tilde{\nu}$ = 2926, 2855, 1767, 1746, 1467, 1367, 1232, 1197, 1119, 1027, 859 cm^{-1}. − MS (EI, 70 eV); *m/z* (%): = 539 (1) $[M]^+$, 497 (100). − HRMS calcd. for $C_{34}H_{53}NO_4$: 539.3975, found: 539.3990.

8-Acetoxy-7-(bromomethyl)-3,5-bis(*n*-decyl)quinoline (7): The diacetate **6** (850 mg, 1.39 mmol) and 15 mL of a solution of HBr in glacial acetic acid (30%) were dissolved in dichloromethane (10 mL). The mixture was stirred at room temp. for three days and then 2 mL of acetic anhydride was added. After removal of the solvent the crude product was purified by column chromatography (silica gel, hexane/ethyl acetate 5:1). Yield: 550 mg (66%) of **7** as a yellow solid; m.p. 35°C. − ^{1}H NMR ($CDCl_3$, 296 K): δ = 8.77 (s, 1 H), 8.05 (s, 1 H), 7.37 (s, 1 H), 4.60 (s, 2 H), 2.99 (t, *J* = 7.9 Hz, 2 H), 2.80 (t, *J* = 7.7 Hz, 2 H), 2.56 (s, 3 H), 1.71 (m, 4 H), 1.31 (m, 28 H), 0.88 (m, 6 H). − ^{13}C NMR ($CDCl_3$, 296 K): δ = 169.4 (C), 151.7 (CH), 143.8 (C), 139.5 (C), 137.3 (C), 136.1 (C), 131.0 (CH), 128.3 (C), 128.0 (C), 127.2 (CH), 33.5 (CH_2), 32.1 (CH_2), 31.9 (CH_2), 31.8 (CH_2), 31.2 (CH_2), 30.7 (CH_2), 29.7 (CH_2), 29.6 (4 CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 29.2 (CH_2), 29.1 (CH_2), 27.4 (CH_2), 22.7 (2 CH_2), 21.0 (CH_3), 14.1 (2 CH_3). − IR (KBr): $\tilde{\nu}$ = 2953, 2918, 2851, 1764, 1470, 1369, 1226, 1212, 905, 694 cm^{-1}. − MS (EI, 70 eV); *m/z* (%): = 559 (0.4) $[M]^+$, 438 (100). − HRMS calcd. for $C_{32}H_{50}BrNO_2$: 559.3025, found: 559.3049. − $C_{32}H_{50}BrNO_2$: calcd. C 68.55, H 8.99, N 2.50; found C 68.29, H 8.66, N 2.35.

1,2-(8-Acetoxy-3,5-bis(*n*-decyl)quinolin-7-yl)ethane (8): A mixture of dibromo bis(triphenylphosphane)nickel (104 mg, 0.14 mmol), tetraethylammonium iodide (716 mg, 2.79 mmol) and activated zinc (274 mg, 4.18 mmol) was stirred in 10 mL of THF under argon for 2 h. The benzyl bromide **7** (520 mg, 0.93 mmol) in 15 mL of THF was added. After 3.5 h at room temp. the solvent was removed in vacuo and the remaining solid was purified by column chromatography (silica gel, gradient: hexane/ethyl acetate 5:1 → 1:2). Yield: 200 mg (45%) of **8** as an orange solid; m.p. 58−60°C. − ^{1}H NMR ($CDCl_3$, 296 K): δ = 8.78 (s, 2 H), 8.06 (s, 2 H), 7.17 (s, 2 H), 3.05 (s, 4 H), 2.93 (t, *J* = 7.7 Hz, 4 H), 2.81 (t, *J* = 7.4 Hz, 4 H), 2.57 (s, 6 H), 1.71 (m, 4 H), 1.60 (m, 4 H), 1.34 (m, 56 H), 0.90 (m, 12 H). − ^{13}C NMR ($CDCl_3$, 296 K): δ = 170.1 (C), 151.3 (CH), 143.0 (C), 139.8 (C), 136.6 (C), 135.0 (C), 132.1 (C), 130.8 (C), 126.6 (CH), 126.0 (CH), 33.4 (CH_2), 32.2 (CH_2), 32.0 (CH_2), 31.9 (CH_2), 31.3 (CH_2), 31.0 (CH_2), 29.8 (CH_2), 29.7 (CH_2), 29.6 (3 CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.3 (2 CH_2), 29.2 (CH_2), 22.7 (2 CH_2), 14.2 (2 CH_3). − IR (KBr): $\tilde{\nu}$ = 3439, 2956, 2923, 2852, 1753, 1469, 1230, 892 cm^{-1}. − MS (EI, 70 eV); *m/z* (%): = 960 (0.1) $[M]^+$, 438 (100). − HRMS calcd. for $C_{64}H_{100}N_2O_4$: 960.7683, found: 960.7612. − $C_{64}H_{100}N_2O_4$: calcd. C 79.95, H 10.48, N 2.91; found C 80.08, H 10.54, N 2.61.

TFA-adduct of 1,2-(3,5-Bis(*n*-decyl)-8-hydroxy-quinolin-7-yl)ethane (9-H_2): The ligand precursor **8** (155 mg, 0.16 mmol) was dissolved

in a mixture of dichloromethane and methanol (15 mL, 1: 1) and 10 drops of trifluoroacetic acid (TFA) were added. After 3 days at room temp. the mixture was taken to dryness. The residue was dissolved in dichloromethane (30 mL), washed with saturated aqueous $NaHCO_3$ (3 × 30 mL), dried ($MgSO_4$) and the solvent was removed in vacuo. Yield: 169 mg (100%) of the TFA-adduct of **9-H$_2$** as an orange solid; m.p. 112°C. – ^{1}H NMR ($CDCl_3$, 296 K): δ = 8.60 (d, *J* = 1.7 Hz, 2 H), 8.26 (br s, 2 H), 7.99 (d, *J* = 1.7 Hz, 2 H), 7.14 (s, 2 H), 3.21 (s, 4 H), 2.86 (t, *J* = 7.8 Hz, 4 H), 2.80 (t, *J* = 7.7 Hz, 4 H), 1.71 (m, 4 H), 1.56 (m, 4 H), 1.32 (m, 56 H), 0.89 (m, 12 H). – ^{13}C NMR ($CDCl_3$, 296 K): δ = 148.6 (CH), 147.4 (C), 137.1 (C), 134.6 (C), 130.9 (CH), 129.4 (CH), 128.0 (C), 125.3 (C), 122.0 (C), 33.5 (CH_2), 32.0 (CH_2), 31.9 (CH_2), 31.7 (CH_2), 31.5 (CH_2), 31.3 (CH_2), 30.3 (CH_2), 29.7 (2 CH_2), 29.6 (3 CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.3 (2 CH_2), 29.2 (CH_2), 22.7 (2 CH_2), 14.1 (2 CH_3). – IR (KBr): $\tilde{\nu}$ = 3311, 2955, 2920, 2849, 1490, 1469, 1421, 1377, 1270, 1147, 676 cm^{-1}. – MS (EI, 70 eV); *m/z* (%): = 876 (56) $[M]^+$, 438 (100). – HRMS calcd. for $C_{60}H_{96}N_2O_2$: 876.7472, found: 876.7425. – $C_{60}H_{96}N_2O_2 \cdot 1.5CF_3COOH$: calcd. C 72.17, H 9.37, N 2.67; found C 72.66, H 9.37, N 2.55.

Preparation of Cryptates [M⊂{(9)$_3$Ga$_2$}]Cl: Ligand **9-H$_2$** (15 mg, 14.3 μmol) and $Ga(NO_3)_3 \cdot H_2O$ (4.8 mg, 18.8 μmol) were dissolved in a mixture of dichloromethane (15 mL), methanol (5 mL) and water (1 mL) in the presence of 50 equivalents of MCl (M = Na, K, NH_4) and the mixture was refluxed for 15 hours. The solvent was removed in vacuum and the remaining solid was subsequently washed with water and methanol (20 mL of each). After drying in vacuum the cryptates were obtained in quantitative yield as yellow waxy solids.

"{(9)$_3$Ga$_2$}": The reaction was performed without addition of MCl. ^{1}H NMR ($CDCl_3$, 296 K): very broad signals at δ = 9.0–7.8 7.3–7.1, 3.2–2.0, 1.9–1.1, 1.0–0.7. – $C_{180}H_{282}Ga_2N_6O_6 \cdot 4CH_2Cl_2$: calcd. C 71.17, H 9.41, N 2.71; found C 70.78, H 9.38, N 2.71.

[Na⊂{(9)$_3$Ga$_2$}]Cl: ^{1}H NMR ($CDCl_3$, 296 K): δ = 8.30 (d, *J* = 1.5 Hz, 6 H), 7.43 (s, 6 H), 6.85 (d, *J* = 1.5 Hz, 6 H), 3.40 (m, 6 H), 2.95 (m, 24 H), 2.62 (m, 30 H), 1.66 (m, 24 H), 1.35 (m, 144 H), 0.90 (m, 36 H). – ^{13}C NMR ($CDCl_3$, 296 K): δ = 152.2 (C), 142.5 (CH), 136.5 (C), 136.2 (CH), 133.8 (C), 132.0 (CH), 126.9 (C), 126.6 (C), 123.5 (C), 33.1 (CH_2), 32.0 (CH_2), 31.9 (CH_2), 31.7 (CH_2), 31.5 (CH_2), 31.4 (CH_2), 31.3 (CH_2), 29.7 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 28.9 (CH_2), 22.7 (CH_2), 22.6 (CH_2), 14.1 (CH_3). – IR (KBr): $\tilde{\nu}$ = 2955, 2924, 2853, 1584, 1462, 1378, 1153, 755 cm^{-1}. – UV-Vis ($CHCl_3$): λ = 274, 328, 342, 421 nm. – Positive FAB MS (3-NBA); *m/z* (%): = 2786 (60) $[Na⊂\{(9)_3Ga_2\}]^+$. – $C_{180}H_{282}ClGa_2N_6NaO_6 \cdot 4.5CH_2Cl_2$: calcd. C 69.11, H 9.15, N 2.62; found C 69.25, H 8.81, N 2.59.

[K⊂{(9)$_3$Ga$_2$}]Cl: ^{1}H NMR ($CDCl_3$, 296 K): δ = 8.29 (s, 6 H), 7.45 (s, 6 H), 7.43 (s, 6 H), 3.28 (m, 6 H), 2.94 (m, 24 H), 2.66 (m, 30 H), 1.67–1.11 (m, 168 H), 0.87 (m, 36 H). – ^{13}C NMR ($CDCl_3$, 296 K): δ = 152.4 (C), 143.1 (CH), 136.6 (C), 136.2 (CH), 134.2 (C), 132.1 (CH), 127.2 (C), 125.1 (C), 123.3 (C), 33.2 (CH_2), 32.0 (CH_2), 31.9 (CH_2), 31.6 (CH_2), 31.5 (CH_2), 31.3 (CH_2), 29.7 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 29.0 (CH_2), 22.7 (CH_2), 14.2 (CH_3). – IR (KBr): $\tilde{\nu}$ = 2955, 2921, 2851, 1583, 1462, 1378, 1153, 754 cm^{-1}. – UV-Vis ($CHCl_3$): λ = 227, 275, 330, 418 nm. – Positive FAB MS (3-NBA): *m/z* (%): = 2804 (100) $[M]^+$. – $C_{180}H_{282}ClGa_2KN_6O_6$: calcd. C 76.12, H 10.01, N 2.96; found C 76.43, H 9.72, N 2.95.

[{NH$_4$}⊂{(9)$_3$Ga$_2$}]Cl: ^{1}H NMR ($CDCl_3$, 296 K): δ = 8.32 (br s, 4 H), 8.29 (s, 6 H), 7.67 (s, 6 H), 7.44 (s, 6 H), 3.25 (m, 6 H), 2.93 (m, 24 H), 2.70 (m, 24 H), 2.64 (m, 6 H), 1.70–1.25 (m, 168 H), 0.87 (m, 36 H). – ^{13}C NMR ($CDCl_3$, 296 K): δ = 152.1 (C), 143.4 (CH), 136.7 (C), 136.1 (CH), 134.4 (C), 132.0 (CH), 127.3 (C), 124.7 (C), 123.5 (C), 33.1 (CH_2), 32.0 (CH_2), 31.9 (CH_2), 31.6 (CH_2), 31.5 (CH_2), 31.2 (CH_2), 29.7 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 28.9 (CH_2), 22.7 (CH_2), 22.6 (CH_2), 14.2 (CH_3). – IR (KBr): $\tilde{\nu}$ = 2954, 2924, 2853, 1584, 1462, 1395, 1377, 1153, 753, 688 cm^{-1}. – UV-Vis ($CHCl_3$): λ = 227, 277, 410 nm. – $C_{180}H_{286}ClGa_2N_7O_6 \cdot 4CH_2Cl_2$: calcd. C 69.96, H 9.38, N 3.10; found C 70.12, H 8.50, N 2.92.

Acknowledgments

Financial support by the *Fonds der Chemischen Industrie* and the *Deutsche Forschungsgemeinschaft* is gratefully acknowledged. We thank Dr. Herbert Röttele for recording the NMR spectra.

[1] [1a] J.-M. Lehn, *Supramolecular Chemistry*, VCH, Weinheim, **1995**. – [1b] E. C. Constable, *Progr. Inorg. Chem.* **1994**, *42*, 67. – [1c] A. F. Williams, *Eur. J. Chem.* **1997**, *3*, 15. – [1d] C. Piguet, G. Bernardinelli, G. Hopfgartner, *Chem. Rev.* **1997**, *97*, 2005. – [1e] M. Albrecht, *Chem. Soc. Rev.* **1998**, *27*, 281. – [1f] R. W. Saalfrank, I. Bernt, *Curr. Opinion Solid State Mat. Sci.* **1998**, *3*, 407.

[2] R. C. Scarrow, D. L. White, K. N. Raymond, *J. Am. Chem. Soc.* **1985**, *107*, 6540.

[3] [3a] M. Albrecht, S. Kotila, *Angew. Chem.* **1995**, *107*, 2285; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2134. – [3b] M. Albrecht, S. Kotila, *Angew. Chem.* **1996**, *108*, 1299; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1208. – [3c] M. Albrecht, H. Röttele, P. Burger, *Chem. Eur. J.* **1996**, *2*, 1264.

[4] [4a] M. Albrecht, O. Blau, *Chem. Commun.* **1997**, 345. – [4b] M. Albrecht, O. Blau, R. Fröhlich, *Chem. Eur. J.* **1999**, *5*, 48.

[5] [5a] E. J. Corey, C. L. Cywin, M. C. Noe, *Tetrahedron Lett.* **1994**, *35*, 69. – [5b] V. A. Grillo, E. J. Seddon, C. M. Grant, G. Aromí, J. C. Bollinger, K. Folting, G. Christou, *Chem. Commun.* **1997**, 1561. – [5c] R. W. Saalfrank, V. Seitz, D. L. Caulder, K. N. Raymond, M. Teichert, D. Stalke, *Eur. J. Inorg. Chem.* **1998**, 1313.

[6] J. Issberner, F. Vögtle, L. De Cola, V. Balzani, *Chem. Eur. J.* **1997**, *3*, 706.

[7] See for comparison: M. Albrecht, *Synthesis* **1996**, 230.

[8] M. Miyaura, T. Ishiyama, H. sasaki, M. Ishikawa, M. Satoh, M. Suzuki, *J. Am. Chem. Soc.* **1989**, *111*, 314.

[9] M. Albrecht, O. Blau, *Synthesis* **1997**, 213.

[10] [10a] M. Iyoda, M. Sakaitani, H. Otsuka, M. Oda, *Chem. Lett.* **1985**, 127. – [10b] M. Albrecht, O. Blau, *J. Prakt. Chem.* **1998**, *340*, 683.

[11] H. Schmidbaur, J. Lettenbauer, D. L. Wilkinson, G. Müller, O. Kumberger, *Z. Naturforsch.* **1991**, *46b*, 901.

[12] [12a] R. W. Saalfrank, I. Bernt, E. Uller, F. Hampel, *Angew. Chem.* **1997**, *109*, 2596; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2482. – [12b] M. A. Houghton, A. Bilyk, M. M. Harding, P. Turner, T. W. Hambley, *J. Chem. Soc., Dalton Trans.* **1997**, 2725. – [12c] S. B. Lee, S. Hwang, D. S. Chung, H. Yun, J.-I. Hong, *Tetrahedron Lett.* **1998**, *39*, 873.

[13] [13a] M. Albrecht, S. Kotila, *Chem. Commun.* **1996**, 2309. – [13b] M. Albrecht, *Eur. J. Chem.* **1997**, *3*, 1466.

Received March 5, 1999
[O99125]